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affected by the change. This explains why the readings of the differential thermometer varied from  $33^{\circ}\cdot 0$  to  $33^{\circ}\cdot 5$  as described in the paper, without producing a corresponding change in the velocity of the anemometer.

For the purpose of obtaining a more correct estimate of the influence of a given increase of heat within the tube, the author introduced into the tube at its lowest extremity, a phial containing eight ounces of water at the temperature of  $100^{\circ}$  Fahr., corked so that no vapour could escape. The result showed that in thirteen observations a quantity of heat equal to an increase of one-tenth of a degree on the scale of the differential thermometer, was equivalent to a mean velocity of the anemometer of 3.6 revolutions per minute, the greatest number being 3.8, the least 3.3 per minute.

These observations render it still more evident, that if a higher temperature within the tube had been the main cause of the revolutions of the anemometer, the variations in their velocity would not have been in such exact relation to the elastic force of the atmospheric vapour, as has been shown to be the case. They also lead to the inference, that the apparent excess of heat within the tube alluded to by the author in his Paper read before the Society in 1855 did not really exist, and to the conclusion that, if such excess had been present, the anemometer would not have been brought to a state of rest by depriving the air of the room of a portion of the moisture ordinarily suspended in it.

II. "On the Relation between Boiling-point and Composition in Organic Compounds." By HERMANN KOPP, Esq. Communicated by Dr. HOFMANN. Received March 20, 1860.

(Abstract.)

The author was the first to observe (in 1841) that, on comparing pairs of analogous organic compounds, the same difference in boiling-point corresponds frequently to the same difference in composition. This relation between boiling-point and composition, when first pointed out, was repeatedly denied, but is now generally admitted. The continued experiments of the author, as well as of numerous other inquirers, have since fixed many boiling-points which had hitherto

remained undetermined, and corrected such as had been inaccurately observed. In the present paper the author has collected his experimental determinations, and has given a survey of all the facts satisfactorily established up to the present moment regarding the relations between boiling-point and composition.

The several propositions previously announced by the author were :—

1. An alcohol,  $C_n H_{n+2} O_2$ , differing in composition from ethylic alcohol ( $C_4 H_6 O_2$ , boiling at  $78^\circ C.$ ) by  $x C_2 H_2$ , more or less, boils  $x \times 19^\circ$  higher or lower than ethylic alcohol.

2. The boiling-point of an acid,  $C_n H_n O_4$ , is  $40^\circ$  higher than that of the corresponding alcohol,  $C^n H_{n+2} O_2$ .

3. The boiling-point of a compound ether is  $82^\circ$  higher than the boiling-point of the isomeric acid,  $C_n H_n O_4$ .

These propositions supply the means of calculating the boiling-points of all alcohols,  $C_n H_{n+2} O_2$ ; of all acids,  $C_n H_n O_4$ ; of all compound ethers,  $C_n H_n O_4$ . The author contrasts the values thus calculated for these substances with the available results of direct observation. The Table embraces eight alcohols,  $C_n H_{n+2} O_2$ , nine acids,  $C_n H_n O_4$ , and twenty-three compound ethers,  $C_n H_n O_4$ ; the calculated boiling-points agree, as a general rule, with those obtained by experiment, as well as two boiling-points of one and the same substance determined by different observers. We are thus justified in assuming that the calculated boiling-point of other alcohols, acids, and ethers belonging to this series will also be found to coincide with the results of observation.

The boiling-points of other monatomic alcohols,  $C_n H_m O_2$ , other monatomic acids,  $C_n H_m O_4$ , and other compound ethers,  $C_n H_m O_4$ , are closely allied with the series previously discussed. A substance containing  $x C$  more or less than the analogous term of the previous class, in which the same number of oxygen and of hydrogen equivalents is present, boils  $x \times 14^\circ.5$  higher or lower; or, what amounts to the same thing, a difference of  $x H$  more or less of hydrogen lowers or raises the boiling-point by  $x \times 5^\circ$ . Thus benzoic acid,  $C_{14} H_6 O_4$ , boils  $8 \times 14^\circ.5$  higher than propionic acid,  $C_6 H_6 O_4$ , or  $8 \times 5^\circ$  higher than cenanthylic acid,  $C_{14} H_{14} O_4$ ; cinnamate of ethyl,  $C_{22} H_{12} O_4$ , boils  $10 \times 14^\circ.5$  higher than butyrate of ethyl,  $C_{12} H_{12} O_4$ , or  $10 \times 5^\circ$  higher than pelargonate of ethyl,  $C_{22} H_{22} O_4$ .

The author compares the boiling-points thus calculated for five alcohols,  $C_nH_mO_4$ ; for six acids,  $C_nH_mO_4$ ; and for sixteen compound ethers,  $C_nH_mO_4$ , with the results of observation. In almost all cases the concordance is sufficient.

The author demonstrates in the next place that in many series of compounds other than those hitherto considered, the elementary difference,  $x\text{C}_2\text{H}_2$ , likewise involves a difference of  $x \times 19^\circ$  in the boiling-point. He further shows that on comparing the boiling-points of the corresponding terms in the several series of homologous substances hitherto considered, many other constant differences in boiling-point are found to correspond to certain differences in composition. Thus a monobasic acid is found to boil  $44^\circ$  higher than its ethyl compound, and  $63^\circ$  higher than its methyl compound; and this constant relation holds good even for acids other than those previously examined, *e. g.* for the substitution-products of acetic acid. Also in substances which are not acids, the substitution of  $\text{C}_4\text{H}_8$  or  $\text{C}_2\text{H}_4$  for  $\text{H}_2$ , occasionally involves a depression of the boiling-points respectively of  $44^\circ$  and  $63^\circ$ ; the relation, however, is by no means generally observed.

The author, in addition to the examples previously quoted, shows that compounds containing benzoyl ( $\text{C}_{14}\text{H}_8\text{O}_2$ ) and benzyl ( $\text{C}_{14}\text{H}_{10}$ ) boil  $78^\circ (= 4 \times 14.5 + 4 \times 5^\circ)$  higher than the corresponding terms containing valeryl ( $\text{C}_{10}\text{H}_8\text{O}_2$ ) and amyl ( $\text{C}_{10}\text{H}_{12}$ ), a relation, however, which is likewise not generally met with. He discusses, moreover, other coincidences and differences of boiling-points of compounds differing in a like manner in composition. Not in all homologous series does the elementary difference  $x\text{C}_2\text{H}_2$  involve a difference of  $x \times 19^\circ$  in boiling-point. The author shows that this difference is greater for the hydrocarbons,  $C_nH_{n-6}$  and  $C_nH_{n+2}$ ; for the acetones and aldehydes,  $C_nH_nO_2$ ; for the so-called simple and mixed ethers,  $C_nH_{n+2}O_2$ ; for the chlorides, bromides, and iodides of the alcohol radicals,  $C_nH_{n+1}$ , and for several other groups; that it is, on the contrary, smaller for the anhydrides of monobasic acids,  $C_nH_{n-2}O_6$ ; for the ethers,  $C_nH_{n-2}O_8$  (which may be formed either by the action of one molecule of a dibasic acid,  $C_nH_{n-2}O_8$ , upon two molecules of a monatomic alcohol,  $C_nH_{n+2}O_2$ , or by the action of two molecules of a monobasic acid,  $C_nH_nO_4$ , upon one molecule of a diatomic alcohol,  $C_nH_{n+2}O_4$ ), and several other series.

The author thinks that the unequal differences in boiling-points corresponding in different homologous series to the elementary difference  $x\text{C}_2\text{H}_2$ , are probably regulated by a more general law, which will be found when the boiling-points of many substances shall have been determined under pressures differing from those of the atmosphere.

“From the observations at present at our disposal it may be affirmed as a general rule, that in homologous compounds belonging to the same series, the differences in boiling-points are proportional to the differences in the formulæ. Exceptions obtain only in cases when terms of a particular group are rather difficult to prepare, or when the substances boil at a very high temperature, at which the observations now at our command are for the most part uncertain. Again, it may be affirmed that the difference in boiling-points, corresponding to the elementary difference  $\text{C}_2\text{H}_2$ , is in a great many series  $=19^\circ$ ; in some series greater, in some series less.”

The author proceeds to discuss the boiling-points of isomeric compounds. He shows that in a great many cases isomeric compounds belonging to the same type, and exhibiting the same chemical character, boil at the same temperature, and that there is no reason why, for the class of bodies mentioned, this coincidence should not obtain generally. On the other hand, different boiling-points are observed in isomeric compounds possessing a different chemical character, although belonging to the same type (*e. g.* acids and compound ethers,  $\text{C}_n\text{H}_n\text{O}_4$ ; alcohols and ethers,  $\text{C}_n\text{H}_{n+2}\text{O}_2$ ), and in isomeric compounds belonging to different types (*e. g.* allylic alcohol and acetone).

The author shows that the determination of the boiling-point of a substance, together with an inquiry into the compounds serially allied with it by their boiling-points, constitutes a valuable means of fixing the character of the substance, the type to which it belongs, and the series of homologous bodies of which it is a term. He quotes as an illustration eugenic acid. The boiling-point of this acid,  $\text{C}_{20}\text{H}_{12}\text{O}_6$ , is  $150^\circ$ ; and on comparing this boiling-point with the boiling-points of benzoic acid,  $\text{C}_{14}\text{H}_6\text{O}_4$  (boiling-point  $253^\circ$ ), and of hydride of salicyl,  $\text{C}_{14}\text{H}_6\text{O}_4$  (boiling-point  $196^\circ$ ), it is obvious that eugenic acid cannot be homologous to benzoic acid, whilst, on the other hand, it becomes extremely probable that it is homologous to hydride of salicyl, and consequently that it belongs rather to the aldehydes than to the acids proper.

The author, in conclusion, calls attention to the importance of considering the chemical character in comparing the boiling-points of the volatile organic bases, and shows the necessity of distinguishing between the primary, secondary, and tertiary monamines in order to exhibit constant differences of boiling-point for this class of substances. He discusses the boiling-points of the several bases,  $C_nH_{n-5}N$  and  $C_nH_{n+3}N$ , and points out how in many cases the particular class to which a base belongs may be ascertained by the determination of the boiling-point.

The comprehensive recognition of definite relations between composition and boiling-point is for the present chiefly limited to organic compounds. But for the majority of these compounds, and indeed for the most important ones, this relation assumes the form of a simple law, which, more especially for the monatomic alcohols,  $C_nH_mO_2$ , for the monobasic acids,  $C_nH_mO_4$ , and for the compound ethers generated by the union of the two previous classes, is proved in the most general manner; so much so, indeed, that in many cases the determination of the boiling-point furnishes most material assistance in fixing the true position and character of a compound.

The author points out more especially that the simplest and most comprehensive relations have been recognized for those classes of organic compounds which have been longest known and most accurately investigated, and that even for those classes the generality and simplicity of the relation, on account of numerous boiling-points incorrectly observed at an earlier date, appeared in the commencement doubtful, and could be more fully acknowledged only after a considerable number of new determinations. Thus he considers himself justified in hoping that also in other classes of compounds, in which simple and comprehensive relations have not hitherto been traced, these relations will become perceptible as soon as the verification of the boiling-points of terms already known, and the examination of new terms, shall have laid a broader foundation for our conclusions.